

**Porous silicon nanoparticles as a nanophotocathode for
photoelectrochemical water splitting**

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Supporting Information

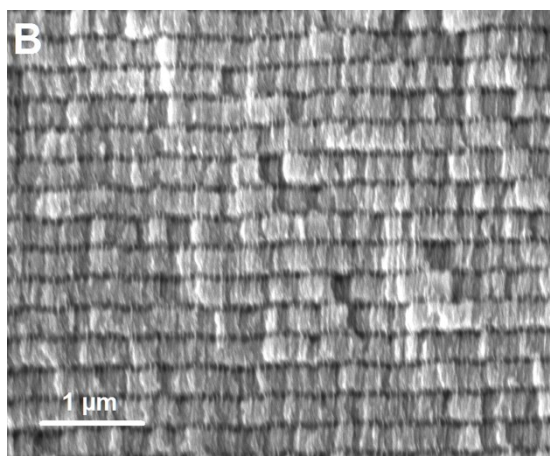
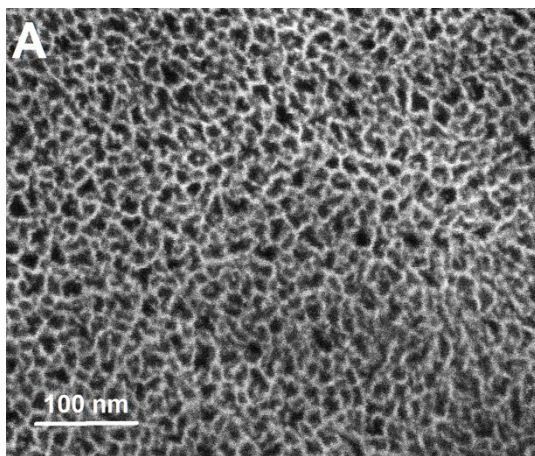


Figure S1. (A) SEM image (Top view) and (B) cross-sectional SEM image showing low and high porosity layers of pSi membrane.

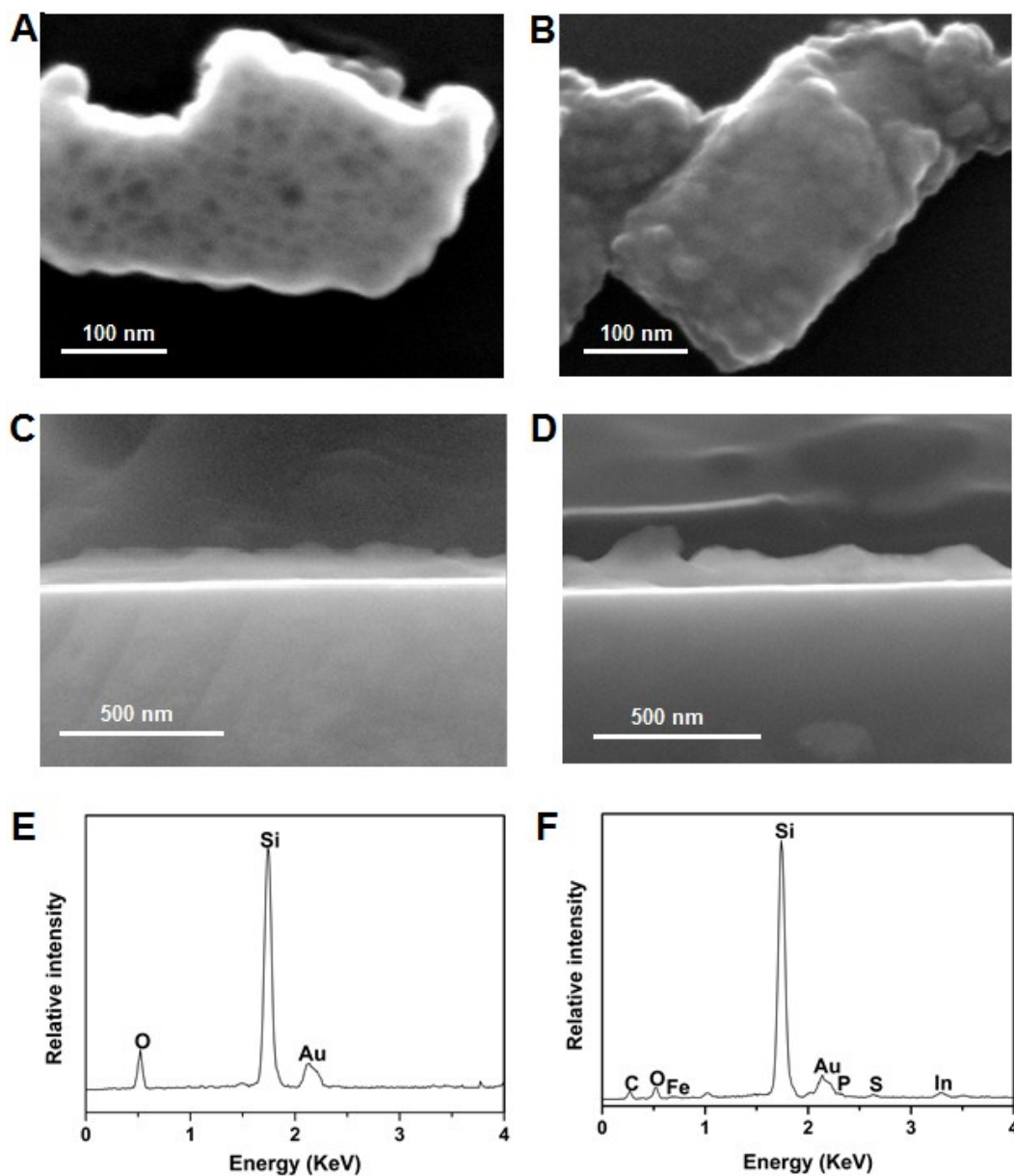


Figure S2. (A) and (B) show SEM images (top view) of AM hydrosilylated pSi NPs and AM hydrosilylated pSi NPs + InP NCs + $\text{Fe}_2\text{S}_2(\text{CO})_6$ catalyst on gold, respectively. (C) and (D) show the cross-sectional SEM images corresponding to (A) and (B), respectively. (E) and (F) show the EDX spectra corresponding to (A) and (B), respectively.

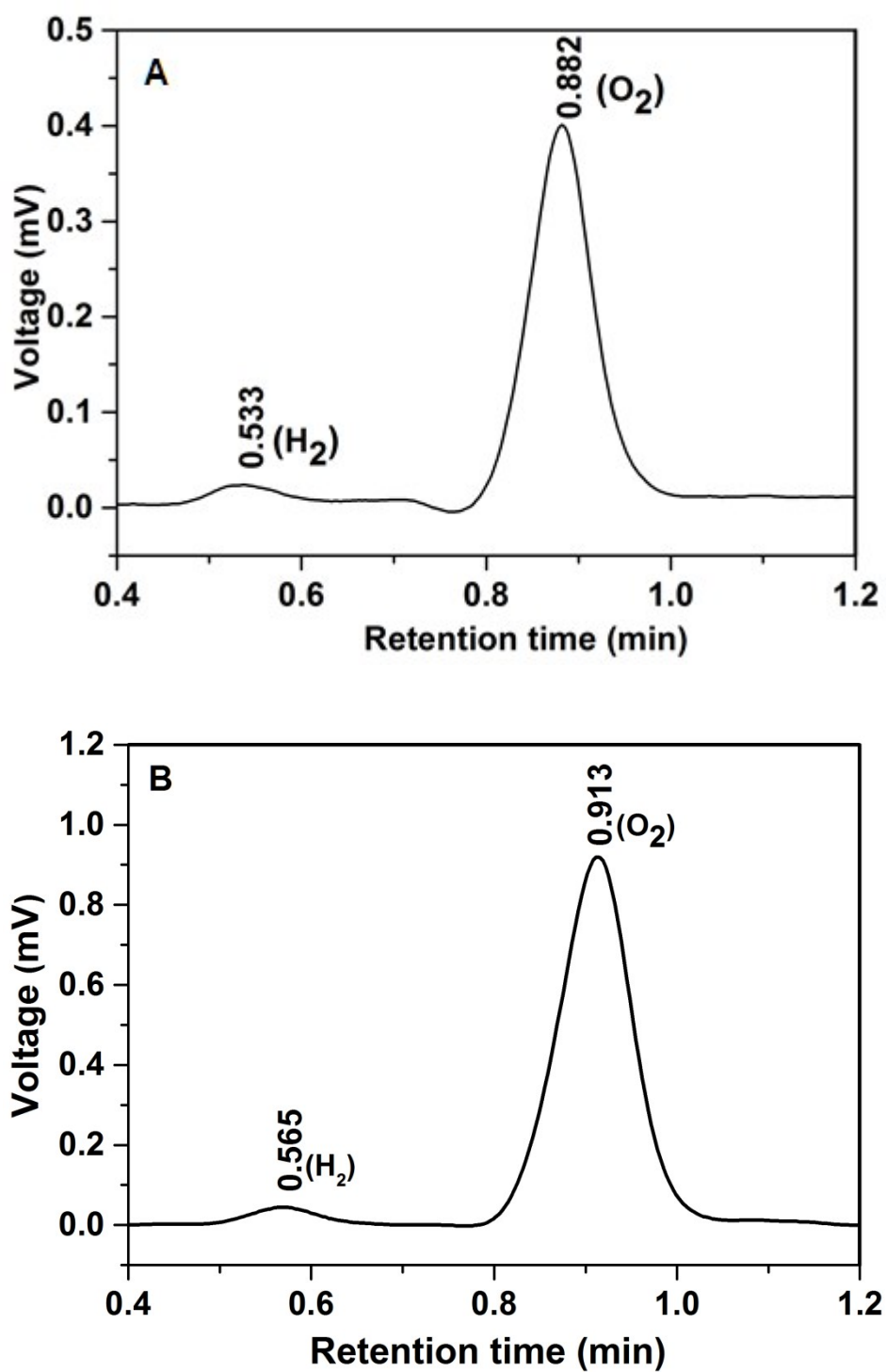


Figure S3. (A) GC analysis of the sample gas from the headspace above the hybrid PEC electrode (310 μ l) and (B) 200 ppm standard H₂ (310 μ l).

Theoretical moles of H₂ produced

According to $R(H_2) = \frac{I}{nF}$, a photocurrent of 2.2 μA should produce 41 nmol of H₂ for 1 h.

$$R(H_2) = \frac{2.2 \times 10^{-6} A}{2 \frac{\text{mol } e^-}{\text{mol } H_2} \times 96485 \frac{C}{\text{mol } e^-}} = 1.14 \times 10^{-5} \times 10^{-6} A \text{ mol } H_2 C^{-1}$$

For 1 h of water splitting reaction = $1.14 \times 10^{-5} \times 10^{-6} A \text{ mol } H_2 C^{-1} \times 3600 s$

(where Charge (C) = Current (A) x Time (s))

Amount of H₂ evolution for 1 h = 41 nmol.

Calculation for moles of H₂ produced from gas chromatography

Area of pure H₂ (310 μl , 200 ppm) = 0.00452 mV min

Consider, 99.5% of pure H₂ has 995000 ppm of H₂.

To convert the area of pure H₂ (310 μl , 200 ppm)

$$\text{into high pure } H_2 = \left[\frac{0.00452 \text{ mV min}}{200 \text{ ppm}} \right] \times 995000 \text{ ppm} = 22.487 \text{ mV min.}$$

Area of high pure H₂ (310 μl) = 22.487 mV min.

Area of sample H₂ (310 μl) after 1 h = 0.00294 mV min

From the areas of pure and sample H₂, the H₂ evolution is calculated based on the formula from Zhang *et al.*¹

$$\text{Amount of } H_2 \text{ evolution} = \frac{\left[\frac{0.00294 \text{ mV min}}{(22.487 - 0.00294) \text{ mV min}} \right] \times 1 \text{ ml} \times \text{mol}}{22.4 \times 1000 \text{ ml}}$$

(where 1 ml is the volume of the headspace.)

Amount of H₂ evolution for 1 h = 5.837 nmol

Reference

1. K. Zhang, D. Jing, C. Xing and L. Guo, *Int. J. Hydrogen Energy*, 2007, **32**, 4685-4691.